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(54) Title: COMPOSITION AND METHOD FOR CLEANING HARD SURFACES		
(57) Abstract The invention relates to a thixotropic composition comprising: (a) at least one acid salt complex; and (b) at least one smectite clay. The composition also optionally comprises a strong acid. The composition is capable of being sprayed, squirted or otherwise applied to the desired locus by means of directional stress. The invention also relates to a method of cleaning a hard surface comprising the step of applying to the hard surface a thixotropic composition of the invention, preferably by spraying.		

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COMPOSITION AND METHOD FOR CLEANING HARD SURFACES

FIELD OF THE INVENTION

5 This invention relates to a composition and method for cleaning hard surfaces. More particularly, this invention relates to a sprayable thixotropic composition containing an acid salt complex and smectite clay and to a method for cleaning hard surfaces using the sprayable composition.

10 BACKGROUND OF THE INVENTION

Hard surfaces formed from porous and non-porous materials, such as ceramics, porcelain, enamel, stainless steel, aluminum, glass, fiberglass, acrylic, gelcoat and the like, that are in continuous contact
15 with water or constantly exposed to the evaporation of hard water develop stains and deposits from the accumulation of materials such as carbonates, sulfates and oxides; salts of calcium, magnesium and other metals and minerals; and the like.

20 A number of different methods, including physical and chemical methods, have been used to clean these stained hard surfaces. Many of these methods have not been fully satisfactory. For example, scrubbing with a pumice stone and/or sanding cloth has been used to clean
25 the hard surface of glazed ceramic tile, such as those used in swimming pools and bath tubs, causing permanent scratches to the glazing. This damage is irreparable and only exacerbates the problem by permitting further penetration of the stains into the ceramic tile.

30 Methods using strong acid cleaners have been utilized to remove the stains on hard surfaces including sanitary ware such as toilets, urinals and the like. Many of

these methods are deficient and create additional problems. The hard surfaces to be cleaned generally contain at least one portion which is vertical and in contact with water. Accordingly, liquid acid cleaners are rapidly dispersed throughout the body of water contained in the sanitary ware and are not concentrated on the porcelain or enamel surface which is to be cleaned. This dilution of the acid cleaner by the water is undesirable and greatly reduces its effectiveness. Furthermore, the dilution requires that the acid be used in highly concentrated form, thus increasing the hazards associated with handling the acid.

Methods using solid acid cleaners do not eliminate these problems since the solid does not adhere to the vertical surfaces and falls to the bottom of the sanitary ware where the solid dissolves slowly.

Solutions have been provided using thickened compositions containing acid which adhere to vertical surfaces when applied. For example in U.S. Patent 4,971,631, a method is disclosed for cleaning hard surfaces by applying a viscous or gelled fluid composition containing mineral-dissolving acid, a lubricant such as glycerin or mineral oil, and a thickening agent such as gelatin or silicon dioxide or mixtures thereof. The disclosed compositions have a viscosity between 1.73 and 76,000 centipoises and a pH of from about 0.01 to 2.0. Unfortunately, thickened compositions containing acid, while adhering to vertical surfaces when applied, are generally too thick to be sprayed because they do not exhibit sufficiently reversible shear thinning or thixotropic behavior.

SUMMARY OF THE INVENTION

This invention is directed to a sprayable thixotropic composition comprising:

- (a) at least one complex acid salt; and
- 5 (b) at least one smectite clay.

The invention is also directed to a method of cleaning a hard surface including the step of applying to the hard surface a thixotropic composition of the invention. The composition is preferably applied by spraying it onto
10 the hard surface.

DETAILED DESCRIPTION OF THE INVENTION

Generally, smectite clays form gel structures for about pH 6 to about pH 13. When an acid is added to the smectite clay gel to lower the pH to a level less than
15 about 6, the gel structure is destroyed. Surprisingly, it has been discovered that the pH of these smectite clay gel structures can be lowered to as low as pH 1 while maintaining the gel structure by adding at least one acid salt complex. These acid salt complex-smectite
20 clay mixtures form sprayable compositions and are particularly useful in a method for cleaning hard surfaces. In addition, the compositions are useful in personal care products where thixotropic behavior is desired.

25 Sprayable Composition

The sprayable thixotropic composition of the invention is a mixture of at least two components:

- (a) at least one acid salt complex; and
- 30 (b) at least one smectite clay.

The stable, sprayable composition may have a pH of from about 1 to about 6, preferably from about 2 to about 4.

The ratio of acid salt complex (in parts by weight) to smectite clay (in parts by weight) in the mixture may be from about 0.1:10 to about 10:0.1, preferably from about 1:10 to about 10:1, and most preferably from about 2:5 to about 5:2.

The sprayable composition of the invention may be formed by:

- (1) hydrating the smectite clay in water using a high speed stirrer and allowing the mixture to gel completely. Gel times are generally of the order of one hour; and then
- (2) adding the solution containing the acid salt complex to the gelled smectite clay and mixing to form a homogeneous solution. When the acid salt complex is added to the gelled smectite clay, the viscosity drops and the mixture may lose its gel structure. This loss in viscosity and gel structure, however, is temporary and is recovered generally within 24 hours and usually within one to five hours. This temporary loss in gel structure is advantageous to manufacturers because it allows for the composition to be easily, quickly and more cheaply pumped into containers without the use of energy-intensive special equipment.

The sprayable composition of the invention exhibits a thixotropic rheological profile such that the composition is a gel appearing solid upon standing yet can behave as thin as water upon shearing. Liquid behavior may thus be exhibited when stress is applied, e.g. by forcing the composition through a nozzle or other orifice. The compositions may thus be referred to as "sprayable", which term is used herein to denote the ability to be sprayed, squirted, or otherwise applied to the desired locus by means of directional stress. Once applied to the locus (e.g. a hard surface to be

cleaned), the compositions of the invention revert to their state of low viscosity, generally adhering well to the surface. This thixotropic rheological profile provides a composition useful in the method of cleaning hard surfaces. In addition, the composition is useful in personal care products, such as skin conditioners, utilizing α -hydroxy acids in formulations, which require a thixotropic rheological profile.

Acid Salt Complex

The acid salt complexes useful in the composition and method of the invention are formed by the complete or partial neutralization of an organic acid with a base to form a complex. The acid salt complex may contain ammonium ions or ions of a metal selected from Group I and Group II of the Periodic Table in combination with at least one carboxylic acid. The acid salt complexes are preferred over the free acid form because they exhibit negligible vapor loss relative to the free acid form and hence are low in odor and retain strong scale and stain removal capabilities.

The acid salt complexes are formed in aqueous solution. The level of complex acid salt in the sprayable compositions of the invention may be from about 0.5% to about 30% by weight, preferably from about 2% to about 20%, by weight, and most preferably from about 5% to about 15% by weight.

Carboxylic acids useful for forming the acid salt complex are formic acid, acetic acid, propionic acid, butyric acid, adipic acid; carboxylic acids of the general formula of $R(C=O)OH$ where R is hydrogen or C_{1-12} alkyl group; α -hydroxy acid of the structure $RCH(OH)-COOH$ where R is hydrogen or C_{1-12} alkyl group; polyhydroxy mono-, di- or tribasic acid such as malic acid, fumaric acid, tartaric acid, citric acid and the

like; dibasic acid, such as oxalic acid, malonic acid, succinic acid and the like. The preferred acid salt complex is ammonium tetraformate.

5 The ratio of acid to ammonium or metal ion is preferably from about 2:1 to about 4:1 (on a chemical equivalent basis of acid to ammonia or metal ion) and most preferably at about 4:1.

10 Even more suprisingly, it has been discovered that strong acids may be optionally added to the mixture of smectite clay and acid salt complex without destroying the gel structure. The strong acids may be added at a level of about 0.5% to about 10%, by weight. Strong acids include both inorganic acids and organic acids.

15 Examples of suitable inorganic acids include hydrochloric acid, hydrobromic acid, hydriodic acid, hydrofluoric acid, sulfuric acid, sulfamic acid, perchloric acid, nitric acid, nitrous acid, phosphoric acid, carbonic acid and peroxy acid such as hydrogen peroxide, and the like. Example of suitable organic
20 acids include monocarboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, benzoic acid and salicylic acid; dicarboxylic acids, such as oxalic acid, phthalic acid, sebacic acid and adipic acid; tricarboxylic acid, such as citric acid; peroxy acid
25 such as peracetic acid; and the like. Hydrochloric acid and sulfamic acid are preferred when ammonium tetraformate is utilized.

Smectite Clay Component

30 Suitable smectite clays include both synthetic and naturally-occurring varieties of swelling clays. Synthetic smectite clays include layer-structured hydrous magnesium silicates such as LAPONITE clay

available from Laporte Industries Limited of Widnes, England. Naturally-occurring varieties include those of the Saponite sub-group (dioctahedral mineral phyllosilicate structure) such as saponite, sauconite and hectorite; and Montmorillonite sub-group (trioctahedral mineral phyllosilicate structure) such as montmorillonite (including bentonite and exchanged bentonite), beidellite and nontronite. Synthetic smectite clays are preferred.

10 Optional Components

The sprayable thixotropic composition may optionally contain other ingredients, provided that the optional ingredients are stable in an acid environment and do not interfere substantially with the rheological behavior of the composition. Optional ingredients include, but are not limited to, surfactants, dyes, fragrances, disinfectants, abrasives, sequestering agents, thickeners, dispersants, solvents, buffer salts and the like. Optional ingredients when the composition will be used in a personal care product include humectants, oils, skin conditioning components and the like.

pH indicators may be added to the solution to identify when the acid has spent its usefulness in cleaning. These indicators include, but are not limited to, modified methyl orange, bromcresol green, methyl red, bromthymol blue, bromcresol purple, phenolphthalein and thymolphthalein.

Method of Cleaning Hard Surfaces

The method of cleaning hard surfaces includes at least the step of applying to the hard surface a thixotropic composition of the invention. The composition is preferably applied by spraying it onto the hard surface.

The compositions may be applied from any of the following containers, which are known *per se* in the art: trigger spray bottles (both foaming and non-foaming variants); directional spouts; so-called flip top cap
5 spouts; containers with narrow mouths; conventional bottles. Sprays and other directional applicators are favoured because of their ease of use.

Because of its thixotropic nature, the composition reforms its gel structure after being sprayed onto the
10 hard surface. This enables the composition to reduce so-called "run-off" from vertical, near vertical and even inverted surfaces.

In another embodiment of the invention, there is provided a method of cleaning a hard surface including
15 at least two steps of:

- (1) forming a thixotropic composition comprising:
 - (a) at least one acid salt complex; and
 - (b) at least one smectite clay; and
- (2) applying the thixotropic composition to a hard
20 surface. Step (2) preferably involves spraying the composition onto the hard surface.

The compositions prepared in accordance with this invention are stable in storage and retain their novel characteristics for relatively long periods of time.
25 The compositions are generally packaged in a container which is designed to facilitate their application. Because of their acidic nature, the compositions are generally not stored in metal containers. The compositions may be applied by filling a flexible
30 plastic squeeze bottle fitted with a directional nozzle or orifice which permits accurate squirting or spraying of a stream of the composition onto the surface of the article to be cleaned. Other suitable containers for the compositions have already been mentioned above.

An optional third step of the method is rinsing or sponging away the composition with water after the scale and/or stain has been removed.

5 Generally, the method of the invention is carried out at ambient temperatures. However, the method may be carried out at elevated temperatures.

10 The composition and method of the invention are useful for cleaning hard surfaces, including both porous and non-porous materials, such as ceramics, stainless steel, aluminum, glass, fiberglass, acrylic, gelcoat and the like. The composition and method of the invention are useful for removing stains and deposits caused by carbonates, sulfates and oxides; salts of calcium, magnesium and other metals and minerals; and the like.

15 The invention is further described in the following examples, which illustrate the composition and method of the present invention. These examples are intended to be illustrative only, and are not to be construed as limiting the scope of the invention.

20 **EXAMPLES**

Example 1

	Components	Level (by weight based on total weight)
25	LAPONITE RD smectite clay	4.5%
	Deionized water	82.5%
	Isopropyl alcohol	4.0%
	Ammonium tetraformate (70% solution)	9.0%

30 The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the

smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained. Then the isopropyl alcohol was added to and mixed with the gel solution. Finally ammonium tetraformate was added to and mixed with the gel solution.

The final composition had a pH of 3.2 and on gelling was successfully sprayed through a hand-operated pump spray.

Example 2

10	Components	Level (by weight based on total weight)
	LAPONITE RD smectite clay	4.5%
	Deionized water	82.2%
15	Dipropylene glycol monomethyl ether	4.0%
	Fragrance	0.3%
	Ammonium tetraformate (70% solution)	9.0%

The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained. Fragrance was dissolved in dipropylene glycol monomethyl ether. The fragrance mixture was then added to and mixed with the gel solution. Finally ammonium tetraformate was added to and mixed with the gel solution.

The final composition had a pH of 3.2 and on gelling was successfully sprayed through a hand-operated pump spray.

Example 3

	Components	Level (by weight based on total weight)
5	LAPONITE RD smectite clay	4.5%
	Deionized water	79.2%
	Dipropylene glycol monomethyl ether	4.0%
	Fragrance	0.3%
	Ammonium tetraformate (70% solution)	9.0%
10	Citric acid	3.0%

The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained. Fragrance was dissolved in dipropylene glycol monomethyl ether. The fragrance mixture was then added to and mixed with the gel solution. Ammonium tetraformate was added to and mixed with the gel solution. Finally, citric acid was added to and mixed with the gel solution.

The final composition had a pH of 3.1 and on gelling was successfully sprayed through a hand-operated pump spray.

Example 4

	Components	Level (by weight based on total weight)
5	LAPONITE RD smectite clay	4.5%
	Deionized water	82.5%
	Dipropylene glycol monomethyl ether	3.0%
	EMPIGEN OH alkyl dimethyl amine oxide (available from Albright and Wilson Ltd., UK)	1.0%
10	Ammonium tetraformate (70% solution)	9.0%

The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained. Dipropylene glycol monomethyl ether and alkyl dimethyl amine oxide were added to and mixed with the gel solution. Finally, ammonium tetraformate was added to and mixed with the gel solution.

20

The final composition had a pH of 3.2 and on gelling was successfully sprayed through a hand-operated pump spray.

Example 5

	Components	Level (by weight based on total weight)
5	LAPONITE RD smectite clay	5.0%
	Deionized water	81.0%
	Ammonium tetraformate (70% solution)	9.0%
	Hydrochloric acid (35% solution)	5.0%
10	The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained.	
15	Ammonium tetraformate (70% solution) followed by hydrochloric acid (35% solution) were added to and mixed with the gel solution.	
20	The final composition had a pH of 1.9 and formed a gel after standing 24 hours. The composition was successfully sprayed through a hand-operated pump spray.	

Example 6

	Components	Level (by weight based on total weight)
25	LAPONITE RD smectite clay	5.0%
	Deionized water	81.0%
	Ammonium tetraformate (70% solution)	9.0%
30	Ortho phosphoric acid (85% solution)	5.0%

The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained.

Ammonium tetraformate (70% solution) followed by ortho phosphoric acid (85% solution) were added to and mixed with the gel solution.

- 5 The final composition had a pH of 3.1 and formed a gel after standing 24 hours. The composition was successfully sprayed through a hand-operated pump spray.

Example 7

10	Components	Level (by weight based on total weight)
	LAPONITE RD smectite clay	1.0%
	Deionized water	81.6%
	Ammonium tetraformate (70% solution)	9.0%
15	Citric acid (anhydrous)	2.0%
	Diethylene glycol monobutyl ether	5.0%
	Dobanic acid	1.0%
	(available from Shell Chemicals, UK)	
	Xanthan gum, "Kelzan T"	0.2%
20	(available from Kelco)	
	Fragrance	0.2%

- The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained. The xanthan gum was hydrated in a separate operation. The fragrance was dissolved in the diethylene glycol monobutyl ether, then the dobanic acid, ammonium tetraformate and citric acid were added to and mixed with this solution. When all the solids had dissolved, the hydrated xanthan gum solution was added, and mixed until a homogeneous solution was formed. This was then added to the hydrated smectite clay.
- 35 The final composition had a pH of 3.0 and could be sprayed or otherwise applied directly onto hard surfaces.

Example 8

	Components	Level (by weight based on total weight)
5	LAPONITE RD smectite clay	0.7%
	Deionized water	57.5%
	Ammonium tetraformate (70% solution)	6.0%
	Citric acid (anhydrous)	1.0%
	Diethylene glycol monobutyl ether	4.0%
10	Dobanic acid	1.0%
	(available from Shell Chemicals, UK)	
	Xanthan gum, "Kelzan T"	0.2%
	(available from Kelco)	
	Light china clay	30.0%
15	Fragrance	0.2%

The composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained. The xanthan gum was hydrated in a separate operation. The fragrance was dissolved in the diethylene glycol monobutyl ether, then the dobanic acid, ammonium tetraformate and citric acid were added to and mixed with this solution. When all the solids had dissolved, the hydrated xanthan gum solution was added, and mixed until a homogeneous solution was formed. This was then added to the hydrated smectite clay. Finally, the light china clay was added and mixed in until a homogeneous paste was produced.

The final composition could be applied directly onto hard surfaces using applicators with narrow openings, e.g. by squirting.

Example 9

This Example illustrates the preparation of a cosmetic gel which contains α -hydroxy acid.

5	Components	Level (by weight based on total weight)
	LAPONITE RD smectite clay	4.0%
	Deionized water	83.55%
	Glycerine	0.75%
10	Sodium lactate	6.5%
	Multifruit acids BSC	5.0%
	(available from Brooks Industries)	
	Dowicil 200	0.2%
15	(available from Dow Chemical Co. Ltd., UK)	

The sprayable composition was prepared by first hydrating the LAPONITE RD smectite clay by mixing the smectite clay with the deionized water using a high speed mixture until a clear gel solution was obtained.

20 When a smooth gel was formed, the remaining ingredients were added in the order shown.

The final composition was a thick, translucent gel with a pH of 4.6 which could be sprayed.

25 Various modifications of the invention, in addition to those shown and described herein, will be readily apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

CLAIMS

1. A sprayable thixotropic composition, comprising:
 - (a) at least one acid salt complex; and
 - (b) at least one smectite clay.
- 5 2. The sprayable thixotropic composition of claim 1 wherein the pH is less than about 6.
3. The sprayable thixotropic composition of claim 1 or claim 2, further comprising a strong acid.
- 10 4. The sprayable thixotropic composition of any one of claims 1 to 3 wherein said acid salt complex is present at a level of from about 0.5% to about 30% by weight.
- 15 5. The sprayable thixotropic composition of claim 4 wherein said acid salt complex is present at a level of from about 2% to about 20% by weight.
6. The sprayable thixotropic composition of claim 5 wherein said acid salt complex is present at a level of from about 5% to about 15% by weight.
- 20 7. The sprayable thixotropic composition of any one of claims 1 to 6 wherein said acid salt complex is formed by the neutralization of an organic acid with a base.
- 25 8. The sprayable thixotropic composition of any one of claims 1 to 7 wherein said acid salt complex comprises:
 - (a) at least one carboxylic acid; and
 - (b) an ion selected from the group consisting of ammonium, Group I metal and Group II metal.

9. The sprayable thixotropic composition of claim 8 wherein said acid salt complex is ammonium tetraformate.
- 5 10. The sprayable thixotropic composition of claim 8 wherein said carboxylic acid is an α -hydroxy acid of the structure $\text{RCH}(\text{OH})-\text{COOH}$ where R is hydrogen or a C_{1-12} alkyl group.
- 10 11. The sprayable thixotropic composition of any one of claims 1 to 10 wherein said smectite clay is a synthetic smectite clay.
12. The sprayable thixotropic composition of any one of claims 1 to 10 wherein said smectite clay is a layer-structured hydrous magnesium silicate.
- 15 13. A method of cleaning a hard surface, comprising the step of applying to the hard surface a thixotropic composition as claimed in any one of claims 1 to 12.
14. A method as claimed in claim 13 wherein the thixotropic composition is sprayed onto the hard surface.
- 20 15. A process for preparing a sprayable thixotropic composition as claimed in any one of claims 1 to 12, comprising the steps of:
- 25 (i) hydrating a smectite clay by mixing said clay with water and allowing the mixture to gel completely;
- (ii) mixing the gelled smectite clay with a solution of an acid salt complex.

16. A sprayable thixotropic composition substantially as described herein with reference to any one of the Examples.
- 5 17. A process for preparing a sprayable thixotropic composition substantially as described herein with reference to any one of the Examples.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/00512

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D3/12 C11D3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 532 066 (PASZEK LEON E. ET AL.) 30 July 1985 see column 4, line 3 - column 5, line 57 see claims	1,2,7,8, 11-14
A	DE,A,38 28 114 (COLGATE-PALMOLIVE CO.) 2 March 1989 see page 8, line 13 - page 9, line 57 see claims	1,7,8, 11,12
A	US,A,4 971 631 (SALLEE KEVIN D. ET AL.) 20 November 1990 cited in the application see claims	1-3,13, 14

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 96/00512

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP,A,0 375 167 (BP CHEMICALS LTD.) 27 June 1990 see page 2, line 1 - line 20 see claims 1-9 -----</p>	1-4,7-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

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